ELECTROCHEMICAL STUDIES OF SOME COORDINATION COMPOUNDS OF HEAVY METALS

BY

BODIE EUGENE DOUGLAS

B.S., The Tulane University of Louisiana, 1944
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AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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ELECTROCHEMICAL STUDIES OF SOME COORDINATION COMPOUNDS OF HEAVY METALS

Until recent years very little had been done to determine the stability of coordination compounds quantitatively, although the results of such measurements are certain to be of value in throwing light on the factors which contribute to stability. Electrochemical studies offer one of the most convenient approaches to the problem of determining the stability of coordination compounds in solution. If sufficient electrochemical data are available and the electrode processes involved are reversible, it is possible to calculate the number of groups attached to the metal ion, the dissociation constant for the complex and the standard potential for the reduction or oxidation of the complex.

Several complexes of manganese were studied with the expectation that the stabilities could be determined for a series of such compounds. The first studies concerned the pyrophosphate complexes formed by manganese(II) and manganese(III). Manganese(II) was oxidized to manganese(III) by titration with potassium permanganate in the presence of an excess of pyrophosphate ion. The potential (vs. the saturated calomel electrode) of a bright platinum electrode in a solution containing equal concentrations of manganese(II) and manganese(III) in the presence of 0.2 M sodium pyrophosphate was found to vary continuously with the pH of the solution. This system was abandoned when it was learned that a similar, but more complete study was soon to be published (1).

Similar potentiometric titrations of manganese(II) with potassium permanganate were carried out in the presence of orthophosphate ion. These titrations were not successful because of the insolubility of the manganese compounds formed and because equilibrium was attained very slowly.

Verdier (2) reported that manganese(II) is oxidized at the dropping mercury electrode in alkaline tartrate solution to give a well-defined anodic wave. This work was repeated since Verdier's data are incomplete, but the oxidation process was found to be irreversible. Under such circumstances no calculations concerning the stability or formula of a complex can be made from the electrochemical data.

The reduction of manganese(II) in the presence of potassium cyanide was reported by Verdier (3) to proceed directly to the metal at the dropping mercury electrode. In the present investigation, the analysis of the polarographic reduction wave for manganese(II) in the presence of concentrations of potassium cyanide greater than 0.7 N indicated that the manganese(II) was reduced reversibly to manganese(I). Potassium hexacyanomanganate(III) in potassium cyanide solution was found to give a reduction wave at the anodic depolarization potential and another wave of equal height at the potential corresponding to the reducton of manganese(II) to manganese(I). The appearance of two reducton waves of equal height for potassium hexacyanomanganate(III) in the presence of potassium cyanide verifies the fact that the reduction of manganese(II) at the dropping mercury electrode in potassium cyanide solution is a one electron reduction. The half-wave potential for the reduction of manganese(II) did not shift with changes in the concentration of potassium cyanide, within the concentration limits necessary for reversible behavior. The half-wave potential should shift significantly with changes in the concentration of potassum cyanide if the reduction proceeded reversibly to the metal as claimed by Verdier. The standard potential for the manganese(II)-manganese(III) couple in the presence of potassium cyanide was estimated to be — 1.08 volts vs. the normal hydrogen electrode. The ratio of the dissociation constants for the two complexes could not be calculated because no data are available to permit the evaluation of the standard potential for the aquated ions.

The investigation of the complexes of manganese indicated

that few of the complexes formed by manganese could be expected to be suitable for electrochemical study. The complexes formed by chromium are more numerous and it was hoped that the stability of these complexes could be determined by the methods used for the manganese complexes. The complexes of chromium(III) with ammonia, ethylenediamine and diethylenetriamine were studied polarographically, but the reductions were found to be irreversible. The α,α'-dipyridyl and o-phenanthroline complexes of chromium(III) were also found to reduce irreversibily at the dropping mercury electrode. However, peculiar current-time behavior was noted on the polarograms obtained for the complexes of α,α'-dipyridyl and o-phenanthroline. The curves were inverted, giving a surge of current as a drop of mercury fell from the electrode and a gradual decrease in the current as the new drop grew. This type of behavior could be explained by an absorption phenomenon where the adsorption effect is greatest at the beginning of the growth of the drop when the rate of increase in surface area is greatest and decreases as the drop grows. The electrocapillary curves were obtained in the presence of the complexes and the corresponding complexing agents, and in the presence of the complexing agents alone. The complexing agents lowered the electrocapillary curves markedly. Although the complexes were present at concentrations of only 0.005 M, these complexes lowered the electrocapillary curves to a correspondingly greater extent. The α,α'-dipyridyl complex gave a particularly large effect. Unlike most capillary-active materials, these complexes and complexing agents were adsorbed at potentials as negative as $-$ 1.4 v. vs. the saturated calomel electrode. Most capillary-active materials are desorbed at less negative potentials.

Potassium hexathiocyanatochromate(III) was found to reduce reversibly to the hexathiocyanatochromate(II) complex at the dropping mercury electrode. The standard potential for the reduction was estimated to be $-$ 0.55 v. vs. the normal hydrogen electrode. The ratio of the dissociation constant for the chromium(III) complex to the dissociation

constant for the chromium(II) complex was calculated to be 4.2×10^{-3}.

No reduction waves were observed in the presence of the complexing agents for the chromium(III) complexes with tartaric acid, potassium oxalate or glycine. The fact that no reduction wave appears for these complexes before the discharge of hydrogen or the indifferent electrolyte can only be interpreted to mean that the overvoltage is very great. The reduction wave reported for chromium(III) in saturated tartaric acid solution (4) could have been due to another element or to a catalytic hydrogen discharge wave. The chromium was reported to be present as an impurity in titanium samples which were being examined polarographically, but no attempt to reproduce this wave using a pure chromium salt was reported.

Cadmium was selected as the next element to be studied because many electrode processes for cadmium are known to be reversible. The half-wave potential for cadmium ion in aqueous solution containing potassium nitrate as the indifferent electrolyte was found to be — 0.575 v. vs. the saturated calomel electrode. In the presence of 28.5% ethyl alcohol (by volume), the half-wave potential was shifted ten millivolts in the positive direction. Such a shift is not too large considering the liquid junction potentials, the changes in activities of the ions present and the possible formation of cadmium ions solvated with ethyl alcohol.

The ethylenediamine, propylenediamine and diethylenetriamine complexes of cadmium were found to reduce reversibly to the amalgams at the dropping mercury electrode. The ethylenediamine and diethylenetriamine complexes showed a coordination number of six in the presence of concentrations of complexing agent from 0.01 to 1 M. The propylenediamine complex also showed a coordination number of six in solutions containing 0.1 to 2 M propylenediamine. From 0.01 to 0.1 M propylenediamine, the coordination number approaches four. The standard potentials for the tris(ethylenediamine), tris-

(propylenediamine) and bis(diethylenetriamine) complexes were estimated to be — 1.26, — 1.26, and — 1.31 v. vs. the normal hydrogen electrode. The dissociation constants for the same complexes were calculated to be 6.7×10^{-13}, 5.4×10^{-13} and 7.6×10^{-15}.

The triethylenetetramine complex of cadmium was also found to reduce reversibly to the amalgam at the dropping mercury electrode. The coordination number for cadmium in the presence of 0.01 to 1 M triethylenetetramine was shown to be four. The standard potential for the triethylenetetraminecadmium(II) complex was estimated to be — 1.31 v. vs. the normal hydrogen electrode. The dissociation constant for the complex was found to be 1.2×10^{-14}.

In the presence of 1 to 2 M pyridine, the complex, $[Cd(py)_4]^{++}$, was found to reduce reversibly at the dropping mercury electrode. The standard potential and dissociation constant for the complex were calculated to be — 0.96 v. vs. the normal hydrogen electrode and 3.2×10^{-3}. From about 0.4 to 1 M pyridine, the complex could be best represented by the formula, $[Cd(py)_2]^{++}$. The reduction potential for this complex is the same as for the complex showing a coordination number of four. The dissociation constant is 7.2×10^{-3}. Below 0.4 M pyridine, the data indicate that a complex having a lower mole ratio predominated.

Polarographic investigation indicated that the complex, $[Cd(SCN)_4]^{=}$, was the predominate species in the presence of 0.8 to 1.0 M potassium thiocyanate. The reduction of the complex was found to be reversible and the standard potential is — 0.97 v. vs. the normal hydrogen electrode. The dissociation constant for the complex is 2.5×10^{-3}. From 0.2 to 0.8 M potassium thiocyanate the species, $[Cd(SCN)_2]^{\circ}$, predominated. The standard potential was found to be — 0.96 v. vs. the normal hydrogen electrode; the dissociation constant was calculated to be 3.1×10^{-3}.

The α,α'-dipyridyl complex was shown to have the formula, $[Cd(dipy)_3]^{++}$, in the presence of 0.01 to 0.04 M α,α'-dipyridyl

in aqueous solution. A complex approaching the formula, $[Cd(dipy)_2]^{++}$, predominated in solutions containing 0.005 to 0.01 M α,α'-dipyridyl. In solutions containing 28.5% ethyl alcohol, the formula for the complex was $[Cd(dipy)_3]^{++}$ in the presence of 0.01 to 0.1 M α,α'-dipyridyl. The standard potentials for the $[Cd(dipy)_3]^{++}$ complex in aqueous solution is — 1.21 v., in 28.5% ethyl alcohol solution the value is — 1.19 v. vs. the normal hydrogen electrode. The dissociation constants in the two media are 3.4×10^{-11} and 1×10^{-10} respectively. The very similar o-phenanthroline complex showed a coordination number of six in aqueous solution in the presence of 0.005 to 0.02 M o-phenanthroline. The standard potential is — 1.35 v. vs. the normal hydrogen electrode and the dissociation constant is 6.4×10^{-16}. In 28.5% ethyl alcohol solution the formula for the complex was found to be $[Cd(o\text{-}phen)_2]^{++}$ in the presence of 0.005 to 0.03 M o-phenanthroline. The standard potential for the reduction of this complex to the metal is — 1.29 v. vs. the normal hydrogen electrode; the dissociation constant is 7×10^{-14}.

Similar to the results which Pfeiffer and Quehl (5) and Brasted (6) obtained with zinc ion, the optical rotation of solutions containing ammonium-d-α-bromocamphor-π-sulfonate was observed to change markedly on the addition of tris-(o-phenanthroline) cadmium (II) complex. If a bond exists between the active anion and the cadmium complex or if the active anion is adsorbed by the complex, the diffusion coefficient for the complex should be changed. It was hoped that this change could be detected polarographically, but the reduction wave for the ammonium-d-α-bromocamphor-π- sulfonate obscured the reduction wave for the complex. The complex also gave a pronounced maximum in the presence of the active anion, interfering further with any possible interpretations.

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VITA

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